All-Solid-State Optical Coolers: History, Status, and Potential

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ABSTRACT

Recent experiments and theoretical models relevant to optical cooling of bulk matter are reviewed. A new derivation of the cooling efficiency, accounting both for the escape probability and the saturation intensity, is developed. Applications to an optical refrigerator and a radiation-balanced solid-state laser are considered. An overview is given of results and ideas pertaining to fluorescent cooling of rare-earth-doped solids, semiconductors, fluids, and other potential cooling materials, including the basic thermodynamics of the process.

INTRODUCTION TO SOLID-STATE OPTICAL COOLING

Optical cooling occurs when a material emits photons of higher average energy than those it absorbs. This process is called anti-Stokes fluorescence. In the case of a solid, the extra energy comes from the absorption of phonons. In essence, heat is converted into light and carried out of the sample, where it is dumped onto some external heat sink. The primary requirement for a material to exhibit this cooling effect, when pumped from the top of a ground set of energy levels to the bottom of an excited set, is that the relaxation back to the ground state is radiative. Nonradiative relaxation results in heating which easily overwhelms the small amount of cooling per radiative cycle. Thus the material must have a nearly 100% fluorescence quantum efficiency. For this reason, materials that lase are good candidates for coolers. In fact a laser cooler is an optically pumped laser running in reverse, converting laser light into broadband radiation rather than the other way around. The first demonstration of laser cooling of a bulk solid was in 1995 with a net temperature drop of 0.3°C at room temperature.[1] The sample was a rare-earth doped fluoride glass originally developed for low-loss optical fibers. The ideal cooling efficiency was calculated to be as large as 3% relative to the absorbed pump light.

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DERIVATION OF THE COOLING EFFICIENCY

Consider a small volume element dV at spatial position **r** that is being optically pumped with incident intensity $I(\mathbf{r})$ in W/cm^2 at wavelength $\lambda = c/\nu$. The population densities (ions/cm^3) in the ground and excited states (manifolds) are N_1 and N_2, respectively, where $N = N_1 + N_2$ is the uniform concentration of active ions doped into the host. Denote the effective absorption and emission cross sections (in cm^2) at the pump wavelength as σ_{AP} and σ_{EP}, respectively, and define the dimensionless ratio[2] $\beta \equiv \sigma_{AP}/(\sigma_{AP} + \sigma_{EP})$ where $0 < \beta < 1$. The radiative and nonradiative rates are the inverses of the lifetimes, $W_R = 1/\tau_R$ and $W_{NR} = 1/\tau_{NR}$, respectively.

In steady state, a rate-equation approach leads to two key equations. First, the time dependence of the excited-state population is described by

$$\frac{dN_2}{dt} = 0 = \frac{I}{h\nu}\left(N_1\sigma_{AP} - N_2\sigma_{EP}\right) - f_{esc}N_2W_R - N_2W_{NR}. \tag{1}$$

The first term on the right describes absorption, the second stimulated emission, the third spontaneous emission, and the fourth nonradiative decay (including both direct multiphonon de-excitation and energy transfer from the excited ions to nonfluorescent impurities). The spontaneous radiation term includes the fractional probability $0 \le f_{esc} \le 1$ that the fluorescence photons ultimately escape from the sample; photons which do not escape are assumed to get reabsorbed by active ions, resulting in no net change in the excited-state population.[3] For simplicity, f_{esc} is taken to be an average value over the entire sample; in detail it depends on **r** both because of the proximity of the pumped volume element to the sample surfaces and because the photons emitted in one volume element are in general absorbed in a different volume element than the one of interest.[4,5] (Note that stimulated photons are assumed to be returned to the pump beam and so no escape fraction is needed in the second term.) Defining the external fluorescence quantum efficiency as

$$\eta_{ext} \equiv \frac{f_{esc}W_R}{f_{esc}W_R + W_{NR}} \tag{2}$$

with $0 \le \eta_{ext} \le 1$, Eq. (1) can be rearranged as

$$N_2/N = \beta(1 + I_s/I)^{-1} \tag{3}$$

where the saturation intensity is $I_s \equiv h\nu f_{esc}W_R/\eta_{ext}(\sigma_{AP} + \sigma_{EP})$.

The second key equation is the rate of thermal energy accumulation in the volume element,

$$\frac{du}{dt} = N_1\sigma_{AP}I - N_2\sigma_{EP}I + \alpha_{back}I - f_{esc}N_2h\nu_FW_R \tag{4}$$

in W/cm^3, where α_{back} is an average background nonsaturable absorption coefficient (in cm^{-1}) which is assumed to be approximately wavelength independent due to nonfluorescent impurities and surface coatings, and $\nu_F = c/\lambda_F$ is the mean fluorescence frequency (including the red shifting due to reabsorption). Noting that the resonant absorption coefficient by active ions is $\alpha_{res} = N\sigma_{AP}$ and defining the total absorption coefficient as $\alpha_{tot} = \alpha_{res} + \alpha_{back}$, we can use Eq. (3) to rewrite Eq. (4) in dimensionless form as

$$\frac{du/dt}{\alpha_{tot}I} = 1 - \left[\frac{\eta_{ext}\lambda/\lambda_F}{1 + I/I_s} + \frac{1}{1 + I_s/I}\right]\frac{\alpha_{res}}{\alpha_{tot}}. \tag{5}$$

The numerator of the left-hand side is the net heating power density while the denominator is the total absorbed power density. Therefore, the negative of this expression defines the relative cooling efficiency which we can rewrite in the form

$$\eta_{cool} = (\lambda - \lambda_F^*)/\lambda_F^{**} \tag{6}$$

where the zero-crossing wavelengths are

$$\lambda_F^* = \frac{\lambda_F}{\eta_{ext}}\left(\frac{\alpha_{tot} + \alpha_{back}I/I_s}{\alpha_{res}}\right) \tag{7}$$

and the slope is normalized by

$$\lambda_F^{**} = \frac{\lambda_F}{\eta_{ext}}\left(1+\frac{I}{I_s}\right)\frac{\alpha_{tot}}{\alpha_{res}}. \quad (8)$$

To make these results meaningful, consider some numerical estimates for Yb^{3+}:ZBLAN. Suppose that we pump near the red-shifted mean fluorescence wavelength of $\lambda_F = 1\ \mu m$ so that $\sigma_{AP} + \sigma_{EP} \cong 5\times10^{-21}\ cm^2$. Then assuming values of $f_{esc} = 75\%$, $\tau_R = 2$ ms, and $\eta_{ext} = 99.5\%$, one finds $I_s = 15\ kW/cm^2$. This corresponds to a 1.5 W pump beam having a cross-sectional area of $(100\ \mu m)^2$, which is readily attainable. In the limit of weak pumping ($I << I_s$), we obtain $\lambda_F^* = \lambda_F^{**} = (\lambda_F/\eta_{ext})(1+\alpha_{back}/\alpha_{res})$. At the first zero-crossing wavelength, α_{back} is negligible compared to α_{res} for a reasonable cooling sample, so that we predict the sample to neither heat nor cool when pumped at λ_F/η_{ext}. On the other hand, as we tune to very long wavelengths, the cooling efficiency does not continue to grow linearly with wavelength as Eq. (6) predicts, because $\alpha_{back}/\alpha_{res}$ becomes significant as $\alpha_{res}(\lambda)$ rapidly declines in value, and so η_{cool} bends over, becoming zero when $(\lambda_F/\eta_{ext})(1+\alpha_{back}/\alpha_{res})$ is again equal to λ. For example, if this second zero crossing occurs at 1055 nm, at which wavelength a 1% doped sample has a resonant absorption coefficient[6] of about 0.002 cm^{-1}, then we find that $\alpha_{back} = 10^{-4}\ cm^{-1}$ using the preceding values of λ_F and η_{ext}. On the other hand, near the peak of the Yb^{3+} absorption spectrum, we can neglect α_{back}, so that $\lambda_F^* = \lambda_F/\eta_{ext}$ and $\lambda_F^{**} = \lambda_F^*(1+I/I_s)$. This implies that the amount of heating is lowered when the pump intensity is near saturation, as has been observed in some experiments at the absorption peaks.[7]

In the remainder of this paper, the history of bulk laser cooling from 1999 to the present is reviewed. For a comprehensive survey of experimental and theoretical work on optical cooling prior to 1999, see Ref. 7. Additional, relatively recent reviews have been also been written.[8,9]

COOLING OF RARE-EARTH-DOPED GLASSES & CRYSTALS

Ytterbium-doped solids

Two different methods have been used to maximize the temperature drop of small samples of the fluorozirconate glass ZBLANP (ZrF_4–BaF_2–LaF_3–AlF_3–NaF–PbF_2) doped with 1–2% Yb^{3+} by weight and suspended in a room-temperature evacuated chamber. Gosnell[10] achieved 65°C of cooling by pumping a 7-mm length of 250-μm-diameter fiber with two passes of 2.2-W, 1015-nm radiation from a titanium-sapphire laser (corresponding to an absorbed power of about 0.26 W). The temperature of the fiber was determined by measuring the fluorescence spectrum and comparing its shape to separately calibrated emission spectra. A fiber is the best geometry for maximizing the ratio of the single-pass absorption length to the mass of a sample. The exponential time constant for the cooldown of the sample was measured to be $\tau = 40$ s, and λ_F^* was found to be 999.3 nm at the zero crossing. A good theoretical fit to the time constant could be obtained using a sample emissivity of $\epsilon_s = 0.54$ calculated from the infrared absorption spectrum of undoped ZBLANP. Ytterbium-doped fibers have also been laser cooled by an Australian group, although a maximum temperature drop of only 13°C was achieved.[9,11] A possible explanation is stray absorption of laser light by the fiber cladding, as a microthermocouple in contact with the cladding measured the temperature drop to be less than one-third that measured by fluorescence thermometry which probes the doped core.

At around the same time as Gosnell's work, 48°C of cooling was achieved by pumping a 6-g cylindrical sample of Yb:ZBLAN with 1.6 W of laser light at 1030 nm.[12] The 10-mm-long sample had dielectric mirrors coated onto its two 12-mm-diameter ends to reflect the pump light (admitted through a small hole in one of the coatings) back and forth inside the sample and thereby dramatically increase the effective absorption length. A fit to the experimental data implied a cavity quality factor of $Q = 120$. In addition, the interior walls of the vacuum chamber were coated with a material that absorbs the Yb^{3+} fluorescence while having a low emissivity of $\epsilon_c = 0.1$ at 3–20 μm thermal wavelengths. The sample temperature was measured using a thermocouple attached to the back of one of the coatings, so that it is shadowed from the

fluorescent radiation. Calculations of the heat load on the sample from the surroundings implied that about half was conductive (rather than radiative), indicating substantial grounds for enhanced thermal isolation. Indeed, Epstein's group has recently improved the apparatus to achieve a sample temperature drop of 88°C below ambient for a 3.7-g cooling element.[13,14] Additional reasons for this increase in cooling were the use of a more powerful pump source, a diode-pumped Yb:YAG laser emitting 9.6 W at 1026 nm, and higher purity ZBLAN. The exponential cooldown time constant was $\tau = 25$ min, which is longer than in Gosnell's experiment mainly because of the increase in sample diameter.[15] The temperature dependence T (in K) of the mean fluorescence wavelength was found to be well fit by $\lambda_F = (1007.8 - T/24.0)$ nm, with a quantum efficiency of $\eta_{ext} = 98.4\%$ that is not as high as one would really like for cryocooling applications.

Comparative studies[16] indicate that an optical cryocooler is expected to exhibit superior performance for a given system mass than mechanical or thermoelectric coolers for applications requiring less than 1 W of refrigeration at an operating temperature between 80 and 200 K. This has recently led to the first demonstration of an optical refrigerator that cooled an external 1.1-g load by 12°C relative to the heat sink.[17] The 7.4-W pump source was a commercial Yb:YAG thin-disk laser operating at 1030 nm. A significant limitation of the dielectric-mirror coatings on the ends of the cooling element was discovered by ray tracing: One quarter of the fluorescence can leak through them at oblique angles of incidence, leading to substantial radiative heating if the load is located behind them. To avoid this, the cooling element was attached to the load via a thermal link that provides high thermal conductance but little transport of the fluorescence radiation. Detailed modeling indicates that an optical refrigerator with this feature would be well suited to micro-cooling, such as a 90-K terahertz detector in a 3-cm^3 system package.[18]

A pumping method that avoids having to place mirror coatings on a sample is to insert the cooling element directly into the recirculating laser cavity. In theory[19] this intracavity scheme should be more effective than use of an external cavity, owing to the small sample absorptivity at typical laser cooling pump wavelengths. In practice, however, the best results to date have only resulted in 9°C of cooling, by placing a Brewster-cut Yb:ZBLAN sample inside a diode-pumped Yb:KYW laser.[20] One potential problem is that a cooling sample introduces absorption, surface scattering, and thermal defocusing losses that alter the laser's performance; in addition, foreign impurities in the sample appear to be producing significant heating.

Studies of Yb^{3+}:ZBLAN double-doped with controlled amounts of Er^{3+} indicate that it is not a likely source of heating.[21] On the other hand, electrochemical purification of ZBLANP and BIG (BaF_2–InF_3–GaF_3–ZnF_2–ThF_4–ZrF_4) glass samples doped with Yb^{3+} indicate that the transition-metal ions Fe^{2+} and Cu^{2+} can generate enough heating by background absorption of the pump light or energy transfer from excited ytterbium ions to prevent net optical cooling.[22] Elemental analysis was performed by resonant laser ablation. Additional measurements on ytterbium doped in BIG, as well as in the fluorochloride glass CNBZn (CdF_2–$CdCl_2$–NaF–BaF_2–$BaCl_2$–ZnF_2), have been performed by a collaborative group in Spain and France.[23] Photothermal deflection spectroscopy between liquid-nitrogen and room temperatures show promising internal cooling efficiencies. However, one would expect any bulk cooling to increase when the pump power is increased, and hence excitation at long wavelengths should result in a reduction in the measured spectral intensity due to thermal depopulation of the upper levels in the ground-state manifold. In contrast, an increase in the long-wavelength signal is observed in the difference spectra. The researchers appear to have misinterpreted this result.

Bulk laser cooling has been observed experimentally for two Yb^{3+} doped crystals.[24] A 2.3% Yb:YAG ($Y_3Al_5O_{12}$) sample placed in an external optical cavity and pumped with 1.8 W of 1030-nm radiation dropped in temperature by 9°C from ambient. This is a promising material because of its high thermal conductivity and hardness, although its large refractive index of $n = 1.83$ tends to promote undesirable fluorescence trapping. The mean fluorescence wavelength, quantum efficiency, and background absorption coefficient had fit values of $\lambda_F = 995$ nm, $\eta_{ext} = 98.8\%$, and $\alpha_{back} = 2.2 \times 10^{-4}$ cm^{-1}, respectively. In addition, a 5% Yb:Y_2SiO_5 crystal cooled about 1°C when pumped in a single pass at 1050 nm.

Photothermal deflection spectroscopy has demonstrated internal laser cooling of three additional materials. The monoclinic double tungstate crystals $KGd(WO_4)_2$, abbreviated KGW, and $KY(WO_4)_2$, abbreviated KYW, doped with 3.5 at.% trivalent ytterbium are found to cool[25] with a fluorescence quantum efficiency of $\eta_{ext} = 98.7\%$, limited in part by a large value for the average index of refraction of $n = 2.02$, and a background absorption coefficient of α_{back} = 0.003 cm^{-1}. Parameters such as the mean fluorescence wavelength are computed by averaging over the three crystallographic axes. The absolute cooling efficiency per unit length can be optimized by selecting the pump absorption axis, reaching the large value 4.8%/cm for the *a*-axis at 1001 nm. A third, low-phonon material, $Yb:KPb_2Cl_5$, was found[26] to have a relative cooling efficiency of 0.2%. The mean fluorescence wavelength was measured to be $\lambda_F = 987$ nm with a promising fluorescence quantum efficiency of essentially 100%.

Nanocrystalline Yb^{3+}-doped yttria (Y_2O_3) has recently been discussed as a possible laser cooling candidate.[27] The key advantage that could be provided by a random nanopowder compared to a bulk crystal of the same material is photon localization by multiple scattering, thereby increasing the effective absorption length. Molecular dynamics simulations also indicate a beneficial broadening of peaks and tails in the phonon density of states. Surface defects might become a significant issue in powders however. The ultimate size limit of a nanopowder is grains containing only a single ytterbium ion each. A Chinese group has proposed investigating such "single molecule" optical cooling, for which the stochastic fluctuations in the absorption and emission become evident.[28]

Laser cooling could be limited in some cases by ionization from the excited state of the dopant ion to the conduction band of the host.[29] For example, the conduction band of sapphire lies only 0.6 eV above the $^2F_{5/2}$ excited manifold of Yb^{3+}, thereby enabling excited-state absorption and subsequent nonradiative relaxation that could preclude laser cooling of $Yb:Al_2O_3$.

Thulium-doped solids

Whereas Yb^{3+} has an energy gap between its ground $^2F_{7/2}$ and excited $^2F_{5/2}$ manifolds of 1 μm, the gap between the ground $^3H_6$ manifold of Tm^{3+} and its first excited $^3H_4$ manifold is about half as large, which doubles the ideal cooling efficiency, $\eta_{cool} = (\nu_F - \nu)/\nu \approx k_B T/h\nu_F$. Here it is assumed that one pumps to the red of the mean fluorescence wavelength by a typical thermal phonon energy $k_B T$, where k_B is the Boltzmann constant and T is the operating temperature of the optical refrigerator, which is taken to be fixed. The first observation[30] of cooling in Tm:ZBLAN only resulted in a 1.2°C temperature drop. Just 40 mW was being absorbed out of a single pass of 1.9-μm pulsed laser radiation from an optical parametric oscillator with an average incident power of 3 W. Subsequently,[3,31] by placing Brewster-cut samples in an external cavity, the cooling was improved to as much as 24°C below room temperature, as measured using a heterodyne interferometric technique and a thermal camera. The mean fluorescence wavelength, quantum efficiency, and background absorption coefficient for the 1 wt.% sample with the lowest temperature drop had fit values of $\lambda_F = 1.803$ μm, $\eta_{ext} = 99\%$, and $\alpha_{back} = 2\times10^{-4}$ cm^{-1}, respectively. The cooldown time constant was $\tau \approx 10$ min for the 4 mm × 4 mm cross-section, 8-mm-long sample.

Various crystalline hosts were also tried but only one, BaY_2F_8, was found to exhibit bulk optical cooling.[32] Its complex emission spectrum has a mean fluorescence wavelength of $\lambda_F = 1.793$ μm, and the quantum efficiency and background absorption were measured to be $\eta_{ext} = 99\%$ and $\alpha_{back} = 4\times10^{-4}$ cm^{-1}, respectively, for a sample doped with 2 wt.% Tm^{3+}. Additional spectroscopic studies of possible ytterbium- and thulium-doped fluoride crystals for fluorescent cooling have been performed by a Russian group.[33]

RADIATION-BALANCED LASING OF RARE-EARTH-DOPED CRYSTALS

In 1999, Steven Bowman at the Naval Research Laboratory proposed a new application of solid-state laser cooling.[34] The rate of anti-Stokes cooling due to spontaneous emission by an ytterbium-doped material could be used to balance the Stokes heating resulting from stimulated

emission by the ytterbium ions. This is called a radiation-balanced or a thermal laser. Such a technique could be used to scale solid-state lasers up to powers of military interest (100 kW cw or more) for jamming infrared heat sensors and even for directed energy weapons. (Currently, solid-state lasers are limited to about 1 kW cw. Even when chilled water is circulated over the surfaces of the laser rod, the heat being generated down the bore leads to large thermal gradients and thus to thermo-optic distortions and depolarization.) The concept is to optically pump at a local peak ν_P in absorption which is intermediate between a local peak ν_L in emission to which the output laser cavity is tuned and the mean spontaneous emission frequency ν_F. From a thermodynamic point of view, one can think of the device as a conventional optically pumped laser that is ganged together with an optical cooler.[35] Radiation-balanced lasing is found to be stable with respect to small changes in the pump wavelength and medium temperature.[36] This requires a specific match between the pump and output laser intensities, making the construction of an amplifier conceptually easier than an oscillator.[37]

A good material for this application would have both large cooling and lasing efficiencies. A spectral analysis of candidate ytterbium-doped hosts indicated the tungstates KGW and KYW to be particularly promising.[2] An early prototype[38] validated the concept for a 2-cm-long Yb:KGW slab end-pumped by 6 continuous-wave (cw) laser diode bars, each generating 20 W at 992 nm. A simple stable resonator was constructed for output lasing at 1050 nm, achieving 9.3 W with a wallplug efficiency of 2.5%. The heat load was measured to be merely 1.6% relative to the absorbed pump power density inside the medium. A recent design[39] is considerably more sophisticated, employing ninety 25-W laser diode arrays to edge-pump an Yb:KGW thin-disk laser, yielding 490 W of quasi-cw output with a 9.4% wallplug efficiency. Fluorescence reabsorption has the effect of red-shifting the mean fluorescence wavelength, which increases the quantum defect and is the principal heating mechanism. Nonradiative losses via energy transfer to trace impurities, together with a calorimetrically measured background absorption coefficient of $\alpha_{back} = 8 \times 10^{-4}$ cm^{-1}, also generate some heat, particularly when lasing is interrupted.

A more traditional host[40] for rare-earth lasers is YAG, and currently the Naval Research Laboratory is building[41] a 2-kW cw Yb:YAG radiation-balanced laser that is end-pumped by thirty-two 1030-nm fiber modules, each outputting 120 W. Another idea is to double-dope a host with two different rare-earth ions, one optimized for laser emission and the other for optical cooling, for example Nd^{3+} and Yb^{3+}, respectively.[42] Some of the laser photons emitted by the first set of ions can be absorbed by the second set of ions to drive the cooler.

PROGRESS TOWARD OPTICAL COOLING OF SEMICONDUCTORS

A good recent discussion of the prospects for optically cooling an intrinsic semiconductor can be found in Ref. 43. One key issue is that the high refractive index (e.g., $n = 3.6$ for GaAs) implies a small escape cone, thereby recycling the luminescent photons which both red shifts the mean fluorescence wavelength and decreases the external quantum efficiency by increasing the probability that a trapped photon will encounter a nonradiative trap such as an impurity. Auger processes are also a potential problem at high carrier excitation densities. At lower densities, surface recombination can become important, although this can be mitigated by surface passivation[44] and by operating at a lower refrigerator temperature than ambient, say 100 K. Use of a large, nearly index-matched, nonabsorbing dome[45] (as is typically done for light-emitting diodes) would improve the extraction efficiency f_{esc}, at the expense of adding a substantial thermal mass to the cooler. Use of a nanogap between the refrigerator heterostructure and a fluorescence-absorbing heat sink has also been suggested.[14] If the vacuum gap is less than 100 nm wide, the total internal reflection would be frustrated and yet the thermal conductivity between them would be minimal. There has also been an experimental report[46] of phonon-assisted upconversion between heavy and light holes in a GaAs quantum well at low temperatures, but only locally within the optically pumped volume, which is not particularly promising for practical refrigeration and the idea appears not to have been followed up further.

Detailed theoretical studies of semiconductor laser cooling have been undertaken by a group at Kirtland Air Force Base.[47] The change in the carrier distribution with temperature has been modeled, as well as the thermal diffusion of phonons. The lattice and the carriers can have distinct temperatures that vary in space and time. They have also suggested multiphoton excitation for pumping a wide bandgap material such as the nitrides with a visible laser.[48] That would avoid use of an expensive ultraviolet laser, at some expense in efficiency. The spectral dependence of the photon recycling has been examined in other theoretical work at Arizona State University.[49]

Anti-Stokes photoluminescence from GaAs/InGaAs *p-i-n* photodiodes can improve the efficiency of photovoltaic solar cells.[50] In another vein, electroluminescent cooling can be used to enhance thermionic refrigeration.[51] Electrons from *n*-doped AlGaAs and holes from *p*-doped AlGaAs are driven into an undoped GaAs quantum well by an applied bias. They can recombine radiatively and the photons can carry heat out of the device. There is no detrimental reabsorption in the GaAs, since the AlGaAs alloys have wider bandgaps than it. Localized optical cooling has also been discussed in connection with electrically pumped thermoelectric devices.[52]

OTHER WORK ON OPTICAL COOLING OF BULK MATTER

Interest in rhodamine (Rh) dyes in solution or thin films as a potential fluorescent cooling material is ongoing, because of the obvious tie-in to work on organic lasers and light-emitting diodes. Their short nanosecond radiative lifetime (in contrast to the millisecond lifetime of rare-earth ions) in principle allows for rapid cooling cycles and hence increased refrigeration power. However there have been no new reports of successful bulk cooling of dyes in the past seven years. In fact, recent modeling[4] is in gross conflict with the previously measured cooling efficiencies. Two key difficulties with solvated dyes is their generally poor photostability under laser irradiation and the added thermal load of the cuvette. A couple of early conference papers[53] continued previous work on dilute solutions (below 10^{-4} M) of Rh101 in acidified ethanol, but this unfortunately means the sample absorptivities are very low. (At higher concentrations, undesired aggregates tend to form. These can be minimized to some extent by adding surfactants, as probed by thermal lensing measurements of the internal quantum efficiency.) Internal conversion and intersystem crossing are minimal for these rigid xanthene species. The mean fluorescence wavelength is $\lambda_F = 604.5$ nm, so that a 632.8-nm helium-neon laser has often been used as the excitation source. Studies have also been made of anti-Stokes fluorescence of Rh101 in silica thin films,[54] but the external quantum efficiency was measured using an integrating sphere to be only $\eta_{ext} = 83\%$ (at the lowest concentration of 0.05 wt.%), which is not large enough to support bulk cooling. A Russian group has proposed using pulsed irradiation at high incident intensities to increase the cooling efficiency.[55]

Local laser cooling in gaseous carbon dioxide has been investigated by photothermal deflection spectroscopy.[56] Energy transfer from CO_2 to N_2 promotes the deactivation of the carbon dioxide molecules. Of course, this means the heat burden is simply transferred to the nitrogen species which store the energy in their long-lifetime excited states, so that the cooling effect is transient and a modulated pumping scheme is used. The gas pressure must be kept low enough to prevent nonradiative collisional deactivation of CO_2.

Laser cooling of nuclear spins by optically pumping the hyperfine levels of quantum dots appears theoretically feasible.[57] This requires low temperatures (3 K) and high magnetic fields (10 T) to remove the spin degeneracy. A red-detuned laser permits resonant flipping of a nuclear spin interacting with an electron spin. A π pulse then reflips the electron spin. Finally spontaneous emission closes the cycle and carries away net energy.

A detailed review of radiation thermodynamics with application to laser cooling has been recently compiled.[58] The entropy lost by the cooling element is more than compensated by the gain in entropy of the light as it is converted from an intense, narrowband laser beam into diffuse, broadband fluorescence. A brief discussion[59] of the energy balance (first law of thermodynamics) for optical cooling assumes that the heat load on the cooler is ambient

blackbody radiation. Application of the second and third laws to the quantum mechanics of the process can be used to derive a fundamental bound on the cooling rate at ultralow temperature.[60] It is found that the maximum rate is proportional to the temperature of the cooling load. A current-voltage analogy proves helpful in interpreting the model.

Similarly, equating photon flux in an optical cooler with electron flux in a Peltier cooler, one can directly compare the performances of the two refrigeration techniques.[61] Other work[16] confirms the key result that anti-Stokes coolers are preferable between 190 K and liquid-nitrogen temperatures for small loads. The advantage of recycling the emitted photons (as is done for the electrons in a Peltier device) is emphasized, although from a thermodynamics viewpoint, this should be done photovoltaically rather than by frequency down-conversion.

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